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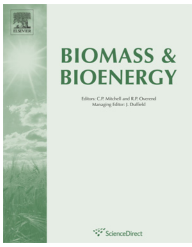

# The effect of torrefaction on the chlorine content and heating value of eight woody biomass samples

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ABSTRACT

This study examined and compared the effect of torrefaction on the heating value, elementary composition, and chlorine content of eight woody biomasses. The biomass samples were torrefied in a specially constructed batch reactor at 260 °C for 30, 60, and 90 min. The original biomasses as well as the solid, liquid, and gaseous torrefaction reaction products were analyzed separately. The higher heating values (HHV) of dry samples increased from 19.5–21.0 MJ $kg^{-1}$ to 21.2–23.2 MJ $kg^{-1}$ during 60 min of torrefaction. In all samples, the HHV increased 9 % on average. Furthermore, the effect of torrefaction time on the biomass HHV was studied. Measurements showed that after a certain point, increasing the torrefaction time had no effect on the samples' HHV. This optimal torrefaction time varied considerably between the samples. For more reactive biomasses, i.e., birch and aspen, the optimal torrefaction time was close 30 min whereas the HHV of less reactive biomasses, e.g., stumps, increased markedly even after a 60-min torrefaction. Another significant observation was that torrefaction reduced the chlorine content of the biomass samples. The chlorine concentration of the solid product dropped in most samples from the original by half or even as much as 90 %. The highest relative chlorine decrease was observed in the *Eucalyptus dunnii* sample, which also had the highest chlorine content of all the studied biomasses. The relative carbon content of the biomass samples increased during torrefaction as the average elementary composition changed from $CH_{0.123}O_{0.827}$ to $CH_{0.105}O_{0.674}$ after a 60-min torrefaction.

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## 1. Introduction

The growing world population and accelerating industrialization keep increasing the energy demand. The concurrent global warming and concerns about the depletion of fossil fuel reserves necessitate the development of sustainable ways to produce energy. Because biomass is considered a carbon-neutral source of energy, partial replacement of coal with biofuels in commercial combustion units lowers the carbon dioxide emissions [1]. However, biomass properties, such as heterogeneous and tenacious structure, hydrophilic nature, and high moisture content are posing challenges to using biomass for energy production.

Torrefaction, i.e., thermal treatment at temperatures ranging from 200 to 300 °C in the absence of oxygen, transforms biomass properties close to those of fossil coal [2,3]. Torrefaction increases biomass bulk density and improves its

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storage and handling properties [4]. Furthermore, torrefaction reduces the biomass moisture content in two ways. First, increasing temperature evaporates the free water in biomass, and at above 200 °C releases the physically bound water [5]. Moreover, biomass loses partly its hydrophilic property as the hydroxyl groups decompose [1]. Torrefaction decreases the biomass oxygen content and increases the relative proportion of carbon, thus improving biomass fuel properties [2]. The vaporization of water and stripping of carbon dioxide (both with zero heating value) increase the biomass heating value. Even a 20-% increase in the biomass heating value during torrefaction has been observed [6]. Torrefaction has also shown to improve the grindability of biomass in terms of lowered energy demand and more spherical particles produced [7,8,9].

Arias et al. [10] have studied the effect of torrefaction on the reactivity and combustion properties of woody biomass and found out that torrefaction affects only to the most reactive hemicellulose components. Because of the low volatile content of torrefied biomass, the activation energy of the first stage of combustion increases [10]. Generally, hardwoods show better reactivity during torrefaction than softwoods because of their higher content of the most reactive hemicellulose component, i.e., glucuronoxylan, or xylan [6]. Compared to coal, the crucial problem in torrefied biomass use is its explosibility and higher flame speed referring to the ignition sensitivity of combustible dust and air mixture and the higher burning velocity of this powder, respectively [11].

This study focused on comparing the behavior of eight woody biomasses during torrefaction. Elementary analyses were conducted on the samples to better understand the changes in biomass during torrefaction. The effect of torrefaction on the biomass chlorine content was examined because fuel derived chlorine compounds may heavily corrode boilers [12,13,14,15] and in flue gas mitigate to the environment. Hydrogen chlorine (HCl) cause acidification [16] and dioxins are a risk to the human health because of their persistence, toxicity, and bio-accumulation resulted from their lipophilicity [17,18]. The effect of torrefaction on biomass chlorine content has not been studied commonly; however, methyl chloride has been detected in the volatile torrefaction products [19]. The torrefaction device in this study is a batch reactor with a relatively large sample particle size and sample volume together with slow torrefaction. Kim et al. [20] and Na et al. [21] have reported similar experimental set-ups.

## 2. Experimental

### 2.1. Materials

The experiments were run with eight woody biomass samples shown in Table 1. The chosen Eucalyptus samples represent globally important wood species and the other biomass samples represent common wood species in Finland.

The biomasses have been chipped, or crushed in the case of stumps, as a part of wood processing and the sample chip

**Table 1 – Biomass samples.**

| Sample | Euca d. | Euca g. | Birch | Aspen | Pine | Spruce | Residue | Stumps |
|---|---|---|---|---|---|---|---|---|
| Species | *Eucalyptus dunnii* | *Eucalyptus grandis* | *Betula pubescens* | *Populus tremula* | *Pinus sylvestris* | *Picea abies* | 97% pine<br>3% birch | 100% spruce |
| Type | Hardwood | Hardwood | Hardwood | Hardwood | Softwood | Softwood | Softwood | Softwood |
| Geographic location | Forestal oriental plantation, Uruguay | Forestal oriental plantation, Uruguay | South-East Finland | South-East Finland | South-East Finland | Eastern Finland | Finland | South-East Finland |
| Date sample obtained | Spring 2012 | Spring 2012 | 15.6.2012 | 15.6.2012 | Spring 2012 | 27.3.2012 | 28.3.2012 | 5.6.2012 |
| Diameter of original cross-section | Not known | Not known | 1–15 cm | 1–15 cm | 15–30 cm | – | <7 cm | – |
| Age | 9–11 years | 9–11 years | Not known | Not known | 70–80 years (final felling) | Not known | 30–40 years (first thinning) | 60–70 years |
| Storage conditions before sampling | Shipped in a container to Finland | Shipped in a container to Finland | Outdoors | Outdoors | Not known | In forest | In forest | In forest |
| Content | Stem wood | Stem wood | Stem wood, sticks, bark | Stem wood, sticks, bark | Stem wood from surface, no bark | Logging waste | Stem wood, bark, pine needles | Roots, foreign matter (soil, stones) |
| Maximum chip dimension | 4 cm | 4 cm | 15 cm (sticks) | 15 cm (sticks) | 8 cm | 12 cm | 12 cm | 12 cm |
| Moisture content, % (mass fraction) | 31.8 | 39.5 | 31.7 | 47.1 | 51.4 | 57.2 | 48.2 | 44.8 |

size varied considerably. The dimensions shown in Table 1 are the maximum dimensions of each chipped species.

The samples were received as rough-grained. Thus, no further crushing was needed and those were used as such in the experiments. Using rough-grained particles is a realistic choice also in large-scale torrefaction applications because the better grindability achieved by torrefaction can then be utilized by crushing the fuel after torrefaction.

After receiving, a sample from each wood species was taken and stored in a freezer to retain its original moisture content until analysis. The remaining samples were dried to prevent molding during storage. Before experiments, each sample was oven-dried at 105 °C according to the European standard EN 14774-3 [22] to remove the moisture.

### 2.2. Test rig

The experiment system shown in Fig. 1 was constructed especially for this project at Tampere University of Technology (TUT). The torrefaction system consisted of an electrically heated oven, a reactor vessel made of stainless steel, and a product gas separation unit. The oven had a heating power of 9 kW and was pre-heated to the selected torrefaction temperature before each experiment. The stainless steel reactor vessel was a cylindrical with an outside diameter of 22 cm and a length of 31 cm. The cover of the reactor vessel was sealed with a graphite gasket and closed with a dense screw fastening. Because of the relatively large sample size, a heater, a coil of steel pipe with closed hot air circulation, was placed inside the reactor vessel to increase the sample heating rate.

At the beginning of each measurement run, the reactor vessel was filled with a sample and placed inside the oven. The gaseous product separation unit was then connected. The reactor vessel and pipeline connections were flushed with nitrogen to ensure inert conditions. A continuous nitrogen flow reported in most torrefaction studies was not used. This enabled collecting the undiluted gaseous reaction products in separate foil bags and analyzing the gas compositions later with FTIR.

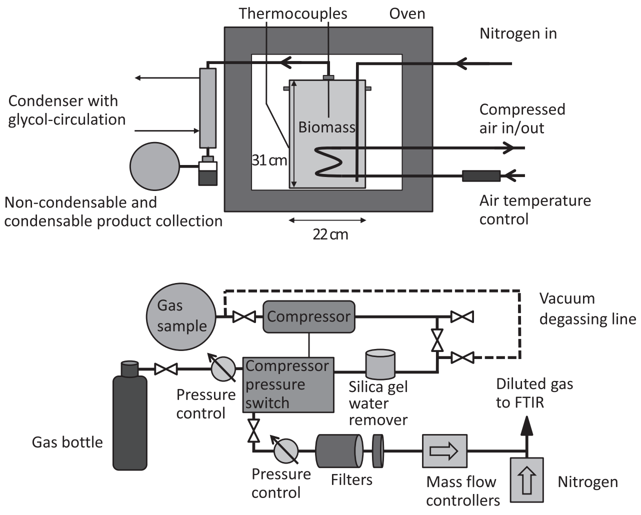

**Fig. 1 – Torrefaction test rig above and the gaseous reaction product pressurization system below.**

Attempts were made to construct a closed setup; however, some gaseous leakage may have occurred. The solid, liquid, and gaseous products were separated from each other during torrefaction. Therefore, it was possible to weigh the separate fractions afterwards and calculate the mass balance for those. The volatile products were separated into condensable and non-condensable fractions in a counterflow condenser with a closed glycol circulation. The condensable fraction of the volatile product was collected into glass bottles immersed in ice water and the non-condensable fraction in the foil bags. The solid reaction product remained in the reactor vessel.

One thermocouple was used to measure the sample's inner temperature at one-second intervals whereas another thermocouple was placed on the reactor side to control the oven temperature. The temperature of the air circulating inside the heater was controlled manually by measuring the temperature of the in flowing air. When a sample reached the targeted 260 °C, the timing began. The sample middle point temperature was chosen to be a constant; however, it oscillated around 260 °C, varying from 257 to 269 °C because of the coarse system control. Furthermore, because of the relatively large sample size, the temperature perhaps fluctuated at the other parts of the reactor vessel even more than was measured.

Quenching the solid residue started upon reaching the torrefaction time by turning off the oven, opening its cover, and switching the heater air circulation from hot to cold. After quenching, all parts of the closed reaction system were weighed for mass balance calculations and all fractions stored until further analysis.

### 2.3. Equations

The mass and energy yields describe how much of the original sample mass and energy content remain in the solid torrefaction product. The mass yield $y_M$ is defined as

$$y_M = \left(\frac{m_{\text{product}}}{m_{\text{feed}}}\right)_{\text{dry}} \tag{1}$$

where $m_{\text{product}}$ is the mass (g) of the remaining torrefied biomass and $m_{\text{feed}}$ is the feedstock initial mass (g), both measured as dry basis (dry). The energy yield is defined as

$$y_E = y_M\left(\frac{\text{HHV}_{\text{product}}}{\text{HHV}_{\text{feed}}}\right)_{\text{dry}} \tag{2}$$

where $\text{HHV}_{\text{product}}$ and $\text{HHV}_{\text{feed}}$ are the higher heating values (MJ $\text{kg}^{-1}$) of torrefied biomass and initial feedstock (dry basis), respectively [23,24].

### 2.4. Experiments

This study focused on the effect of torrefaction on the elemental composition and fuel properties of woody biomasses. Furthermore, the effect of torrefaction time on mass and energy yields was studied. Two torrefaction times were used for each sample. All the samples were torrefied at 260 °C for 60 min, and the second torrefaction time depended on the relative reactivity in the first experiments. The more reactive samples, i.e., those with a high mass loss, were torrefied for

30 min and the less reactive samples, i.e., those with a little mass loss, for 90 min.

Because wood is a poor conductor of heat, it took relatively long for temperature to rise in a sample, despite the preheated oven and the internal heat source. Attempts were made to maintain the rise from room temperature to torrefaction temperature uniform in time, but it varied between 62 and 81 min. The sample volume too was chosen constant, but because sample bulk densities varied, so did the masses between 800 and 1600 g.

### 2.5. *Analyses*

Solid, liquid, and gaseous reaction products were analyzed separately. The solid materials were analyzed by Enas Co. The analyses were run on both the original biomass samples and the solid reaction products of 60-min torrefaction. These analyses comprised ultimate and proximate analyses, ash melting behavior, bulk density, and the concentrations of following the metals: sodium, potassium, calcium, magnesium, silicon, phosphorus, iron, aluminum, and titanium, and the following heavy metals: cadmium, thallium, mercury, antimony, arsenic, chromium, cobalt, copper, manganese, nickel, vanadium, lead, tin, and zinc. Furthermore, the samples were fractionated with water, acetate, and hydrochloric acid to determine the solubility of sodium, potassium, calcium, magnesium, silicon, phosphorus, iron, aluminum, titanium, manganese, and chlorine in them. The reaction products from 30- and 90-min torrefaction were analyzed only for higher and lower heating values. The analyses were not replicated.

The gaseous reaction products were analyzed at TUT. The qualitative and quantitative content of gases were measured with a Gasmet DX4000 Fourier transform infrared spectroscopy (FTIR) analyzer. Before analysis, liquid impurities were filtered out from gas samples, and the gas was pressurized and diluted with gaseous nitrogen (the gas pre-treatment system is shown in Fig. 1). Because the FTIR analyzer does not detect biatomic homonuclear molecules, e.g., nitrogen, gas content could not be directly measured; instead, it was iterated by the least square method.

The chlorine content of the selected liquid products was analyzed by the Institute for Environmental Research at University of Jyvaskyla.

## 3. Results and discussion

### 3.1. *Chlorine content and liquid products*

The most significant experimental result was that the biomass chlorine content decreased during torrefaction. The elementary chlorine content (Fig. 2) dropped markedly in nearly all samples during a 60-min torrefaction, except for the pine sample, which retained its initial chlorine concentration. However, this chlorine concentration was the lowest of all the samples and linked perhaps to the low bark content in the pine sample. The greatest relative decreases in chlorine concentrations were measured for both eucalyptus samples, which originally had the highest chlorine content of all the samples. Torrefaction reduced as much as 90 % of the initial chlorine in the *Eucalyptus dunnii* sample.

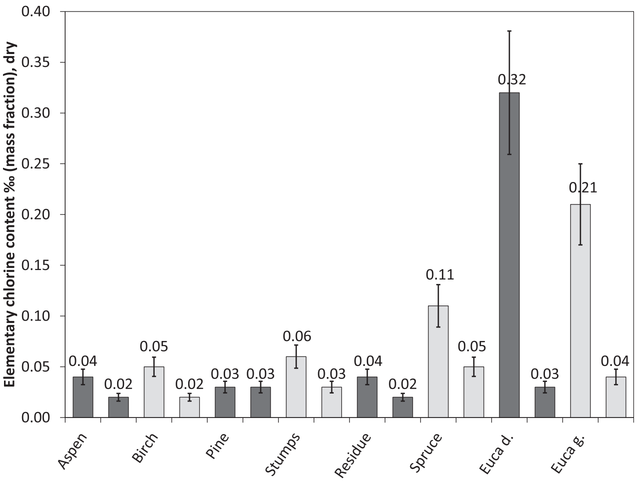

**Fig. 2 – The elementary chlorine content of the original samples (left columns) and the solid products of a 60-min torrefaction (right columns).**

It is not commonly known how chlorine is bound in biomass [25] but it can be largely extracted from various biomasses by leaching with water [26,27]. According to the conducted fractionation analyses, chlorine in experimented biomass samples was mostly in water soluble form, e.g., in original Eucalyptus samples over 95 %. Biomass chlorine reduction in pyrolysis has been frequently studied in connection with alkali release [25,28].

Dioxins, the general name of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), are generally formed according to the following general reaction equation [29]

$$Cl_2 + \text{organic molecules} \rightarrow \text{chlorinated molecules (e.g. PCDD/Fs)} \quad (3)$$

The formation of PCDDs and PCDFs is the most efficient at temperatures around 300 °C [30]. Molecular chlorine needed in the reaction (3) can be formed through the known Deacon reaction [31]

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2 \quad (4)$$

which can be catalyzed by elemental copper or certain copper components [29,31]. The elementary copper content in the original experimented wood samples was between 0.73 and 3.6 mg kg$^{-1}$ of dry sample.

Sulfur has been detected to inhibit dioxin formation by reducing both the $Cl_2$ levels and copper-catalyst levels [31,32]

$$SO_2 + Cl_2 + H_2O \leftrightarrow SO_3 + 2HCl \quad (5)$$

$$CuO + SO_2 + \frac{1}{2}O_2 \leftrightarrow CuSO_4 \quad (6)$$

The thermodynamic equilibrium constants of the reaction (5) for the temperature range of 0–900 °C in Ref. [31] reveal that the reaction towards the products is favored at lower temperatures. However, the low amount of sulfur present in the experimented samples, at maximum 0.04 % of the dry sample mass, considerably limits the reactions (5) and (6). In general, the fuel molar ratio between sulfur and chlorine higher than 4 indicates low risk and less than 2 high risk of corrosion in a boiler [14]. In reference to this, the analysis results indicated a high risk of corrosion for both original Eucalyptus samples. On the contrary, after torrefaction all the experimented samples had a low risk of corrosion.

Björkman and Strömberg [16] have determined how four biomasses with relatively high chlorine content (0.18–0.79 % of total weight) lost chlorine 0–10 % and 3–23 % of the initial weight during pyrolysis at temperatures 200 and 300 °C, respectively. Jensen et al. [25] have reported 50 % release of total chlorine in straw between pyrolysis temperatures 200 and 300 °C and it is suggested in the article that at the temperature range of 200–400 °C the chlorine is released as HCl or potassium chloride (KCl).

The equations in this chapter describe the biomass chlorine reactions at experimented torrefaction temperatures. Based on these equations, it is reasonable to claim that torrefaction can theoretically affect to the biomass chlorine content. The presented results of other studies further support the chlorine reduction behavior of torrefaction.

The analysis of all the gaseous torrefaction products revealed only a hint of chlorine in the form of HCl. Therefore, four chosen liquid products were also analyzed. The literature reports various analyses of liquid torrefaction yield [6,8], yet chlorine content has not been measured in those studies. The chlorine content analyses were conducted for the liquid products of pine, spruce, euca d., and euca g. of 60-min torrefaction. The samples were selected because they represented extreme chlorine reduction behavior among the tested samples. In all reaction products, only pine registered the total measured chlorine as equivalent to that of its initial original sample. For the other samples, a significant proportion of the original chlorine content was not detected in the analyses of solid and liquid reaction products, as shown in Fig. 3.

The following may explain why all chlorine could not be detected. First, the methods used to analyze especially gaseous and liquid products may have been unsuitable for detecting all the possible chemical chlorine compounds. For example, the FTIR cannot discriminate chemical components from each other if the absorption spectrums of those components are overlapping. Second, sampling may have been selective due to the segregation of the gaseous and liquid products in the sampling containers. For example, some volatile compounds may have condensed on foil bag inner surfaces instead of in the liquid collection system. Third possibility is that during torrefaction some chlorine escaped from the system as gas. According to the United States Environmental Protection Agency [33] HCl has "an irritating, pungent odor", but during the experiments it was impossible to discriminate the odor of HCl from the dominant odor of tars.

### 3.2. *Heating value*

An important question in torrefaction research is how much the process can improve the heating value of biomass. In this study, the higher heating value (HHV) increased 9 % on average in all the samples. The HHV of the original biomasses were between 19.5 and 21.0 MJ kg$^{-1}$ and after a 60-min torrefaction between 21.2 and 23.2 MJ kg$^{-1}$. The biomass specific heating value increased with torrefaction time, i.e., when the mass loss increased (the measured HHV of the original biomasses and the solid reaction products shown as a function of mass loss in Fig. 4 (upper points)). The uncertainty of the heating value analysis was reported as 1 %. The uncertainty of the O to C-ratio is not presented as the uncertainty of this analysis was not reported.

Clear differences were observed in reactivity between hardwoods and softwoods. The former, birch and aspen, reacted readily, producing lower mass yields and more volatiles than the latter. Consequently, torrefaction improved most the heating values of the hardwoods.

According to an accepted mass and energy balance for torrefaction, a solid torrefaction product contains 90 % of its

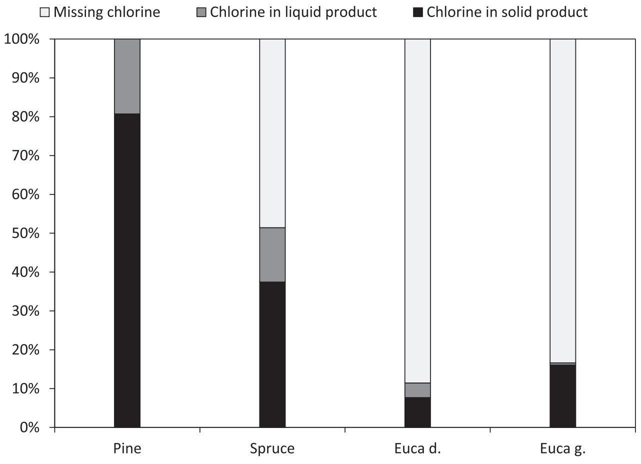

**Fig. 3 – The proportions of detected chlorine in solid and liquid products of total chlorine content in selected original biomasses.**

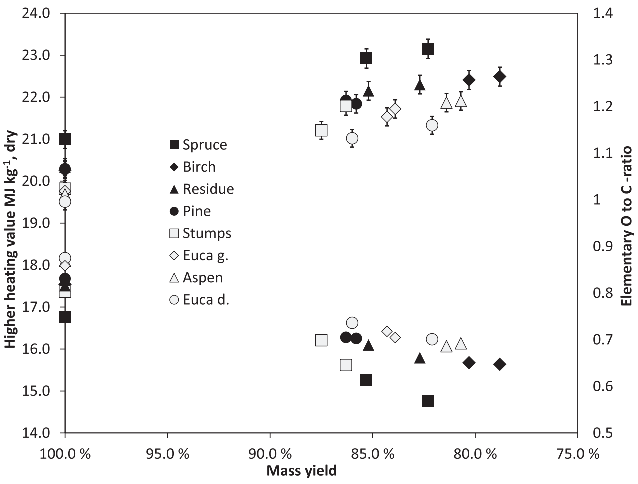

**Fig. 4 – The biomass higher heating value (MJ kg$^{-1}$, dry) as a function of solid mass yield in torrefaction (upper points) and the biomass elementary O to C-ratio as a function of solid mass yield in torrefaction (lower points).**

initial biomass energy but only 70 % of the initial mass; the ratio of energy to mass yield is thus 1.3 [34]. Such positive results were achieved neither in this study nor have they generally appeared in studies presented in literature [35]. In this study, the mass yield of a 60-min torrefaction varied from 78.8 to 87.5 % and the maximum ratio of energy to mass yield, i.e., 1.11, was measured for aspen and birch.

The heating values of the hardwoods, aspen and birch, were almost the same with both torrefaction times of 30 and 60 min. Therefore, for those biomasses the optimal torrefaction time was closer to 30 min. However, as far as the ratio of energy to mass yield is concerned, the less reactive stump sample benefited from longer torrefaction time. After a 90-min torrefaction, its HHV was 0.6 MJ $kg^{-1}$ higher than after a 60-min torrefaction.

Moisture content is one important fuel property. The total moisture content of the original biomasses varied between 31.7 % and 57.2 % of the total mass. However, after torrefaction the moisture content was between 0.7 % and 1.8 %. The uncertainty of moisture content analysis was reportedly 5 %.

The fuel oxygen content is related to its combustion properties. The biomass elementary O to C-ratio decreased in torrefaction, as shown in Fig. 4 (lower points). The average elementary content of the biomass samples changed from $CH_{0.123}O_{0.827}$ to $CH_{0.105}O_{0.674}$ in the 60-min torrefaction, indicating an increase in the biomasses' relative carbon content. The uncertainty of C and H analysis was reportedly 1 % and 2 %, respectively. The decrease in the O to C-ratio results in an increase in the biomass heating value.

### 3.3. *Other fuel properties of the solid products*

The nitrogen and sulfur contents of the solid products were below those suggested by van Loo and Koppejan [12] to cause problems during industrial combustion. The biomass volatile content was analyzed according to the European standard EN 15148 [36]. In torrefaction, the volatile content of the samples decreased between 7 % and 10 %, yet the volatile content remained between 70 % and 80 % of the dry sample mass. This is higher than the coal values, 17–48 % [37]. The uncertainty of the volatile analysis was reportedly 1 %.

Ash melting behavior was analyzed for the original biomass samples and the solid products of the 60-min torrefaction. Four different temperatures were measured in an oxidative atmosphere: deformation temperature, sphere temperature, hemispherical temperature, and fluid temperature. The critical temperature descriptions are given in the literature [38]. According to the analysis results of the experimented biomasses, the critical temperatures of most samples were above the detection limit of 1450 °C. Therefore, the effect of torrefaction cannot be clearly observed. Nevertheless, the critical temperatures of experimented wood samples registered in the same range or even higher than those of coal [39,40]. There is no unambiguous relation between the ash melting behavior in analysis and in actual boiler; however, those have some connection [39]. Therefore, in co-combustion the reactions between different ashes can be detected only experimentally and even a small proportion of molten ash can cause problems in combustion.

According to the conducted experiments, torrefaction do not have any unambiguous influence on the biomass ash content. The ash contents of the original biomasses and solid products of a 60-min torrefaction were measured after burning the samples at 815 and 550 °C. The ash contents varied between 0.3 % and 4.0 % of the dry sample mass, which is again below the coal values, 6–28 % [19].

Torrefaction had no clear effect on the metals concentrations listed in Section 2.5, except for iron, whose concentration decreased in all samples. Bear in mind though that metal concentrations are not crucial in fuels; their chemical interreactions are the decisive factor. The above listed heavy metals concentrations were negligible compared to the reference values for coal [41], except for those of manganese. At all points, its concentration was almost same as or even higher than the coal reference values.

### 3.4. *Gaseous products*

The gaseous reaction product masses varied from 3.1 % to 5.4 % of the original sample masses. Here, the losses during torrefaction, 2.3–4.1 % of original sample masses, are assumed to be gaseous and are added up. According to the FTIR measurements, the average gas content was 79 % of carbon dioxide, 21 % of carbon monoxide, and a trace of methane. Variations between different samples were a few percentage points. The lower heating value of the gaseous products was a maximum of 2 kJ $kg^{-1}$ or 3.3 kJ $m^{-3}$ n, which is negligible compared, e.g., to methane (50 MJ $kg^{-1}$ or 33 MJ $m^{-3}$ n). Thus the combustion of the non-condensable torrefaction product alone is not profitable.

## 4. Conclusion

In torrefaction experiments with woody biomass samples, hardwoods and softwoods behaved differently. The hardwood samples were the most reactive as their energy densities increased most during torrefaction. The HHV of all the samples increased from 19.5–21.0 MJ $kg^{-1}$ to 21.2–23.2 MJ $kg^{-1}$ during a 60-min torrefaction at 260 °C. However, the energy densification of biomass by a factor of 1.3 that is commonly reported in the literature was not achieved. The highest achieved ratio of energy to mass yield was 1.11 for aspen and birch. Furthermore, the heating values of gaseous products were negligible.

The effect of torrefaction on biomass chlorine content has not been widely reported in the literature. It is presented in this study how the chlorine concentration of the experimented biomass samples dropped during torrefaction. The highest reduction in chlorine content, 90 %, was observed in the *E. dunnii* sample. The chemical reactions of chlorine at torrefaction temperatures are shown in chapter 3.1. Chlorine in biomass is theoretically reactive at torrefaction temperatures; however, better analytical methods are required to experimentally determine this phenomenon precisely.

Furthermore, torrefaction improved also other biomass properties. The elementary O to C-ratio decreased, indicating better combustion properties and the increase of heating value. The ash melting behavior of solid torrefaction products was comparable with that of coal and the total ash content of solid products was well below the respective coal values. However, the behavior of ash in a solid torrefaction product during combustion must be studied experimentally.

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